

AD 682875

TRANSLATION NO. 372

DATE: 9 Feb 1954

(1)

DDC AVAILABILITY NOTICE

~~This document is subject to special export
control and is not to be distributed to foreign
persons or organizations without prior approval of the
Department of Defense. It is classified as SECRET
under Executive Order 11652, 1954. It is being
classified SECRET, Fort Detrick, AR 682875-1,
Frederick, Md. 21701.~~

MAR 5 1969

JP

DEPARTMENT OF THE ARMY
Fort Detrick
Frederick, Maryland

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va. 22151

by M. Lepin and S. Wosnesensky - (Moscow)

Kolloid Zeitschrift 49, 288-96 (1929)

Translated by

J.C. Arnell

Defence Research Chemical Laboratories, Ottawa.

The following research was carried out in part as graduate work¹

¹ No. 228 (April 1918) of the Index of the Moscow Commerce Institute

by M. Wosnesensky under the direction of Prof. Schilow in the year 1918 and later carried on in collaboration with Miss L. Lepin. The work nevertheless has been neither completed nor published. Since then more researches have appeared on the subject and it may be mentioned in the first place among them the treatment of Mecklenberg². Because our work and the results

² Mecklenburg, Zeitschr. f. Elektr. 31, 468 (1925)

of Mecklenberg differ substantially, we have considered it fitting to publish our work, which at this time has been supplemented by new experiments.

Although our work concerns the adsorption of a gas mixed with an air stream, yet our results are of other practical uses, such as filtration, leaching, adsorption by ground, etc. Mutatis mutandis the same regularities are valid also for the methods which form the basis of the counter-current principle.

AD 582875

I. Procedure and apparatus

Work has been done, on the one hand on the course of adsorption with time of a gas mixed in an air stream and on the other hand on the spatial distribution of the adsorbed gas in the adsorption layer, etc. in order to study the residual concentration in the streaming air. To this end we had the adsorbing layer in separate sections, that is divided into separated tubes and inserted between the same measuring apparatus with which at a chosen point a gas analysis could be carried out. Small tubes with reagent papers, which could be inserted between the sections as well as at the end of the whole apparatus, allowed the appearance of the gas to be recognized at different places along the bed, corresponding to the consideration that progressive saturation of the adsorbent occurred and with it the protective action of a single length ceased.

We have used different kinds of activated charcoal for the adsorbent and chlorine as the gas. The apparatus was constructed in the following manner: The velocity of the air-chlorine stream was regulated with a rheometer. Both gases after mixing in a large spherical flask entered through a two-way cock either into the main apparatus or into a long branching tube, which offered exactly the same resistance to the air stream as the whole charcoal layer. This tube allowed the gas stream to be regulated before the experiment and to be conducted unchanged into the apparatus at the beginning of the experiment.

The gas measuring devices consisted of flasks of 2 liter capacity with ground glass stoppers and could be shut off by turning two two-way cocks

without interrupting the air stream. A funnel with a glass stopper allowed a KI solution to be run in without opening the flask. The iodine so liberated was titrated with thiosulphate.

The apparatus usually contained 6 or 7 sections, each of them consisted of a glass tube 4 cm. diameter and 12 cm. long that contained an effective 10 cm layer of charcoal which was covered at both ends with perforated platinum plates. For downward flow the tubes were provided with glass stoppers and connecting tubes, for upward flow they narrowed in a ball fitting connecting piece.

With this apparatus we have carried out the following series of experiments:

1. We have determined the spatial distribution of the chlorine in the gas phase along the entire charcoal bed at the moment of the exhaustion of the protective action. This is done by the simultaneous shutting off of all the measuring devices immediately after the appearance of chlorine at the end of the whole apparatus.
2. We have followed with the course of time, the concentration of the chlorine in the flowing air at different places in the absorbing bed.
3. The end of the protective action at different places in the charcoal bed was noted that is the velocity of progress of the first trace along the adsorbing layer was determined.
4. By weighing a single tube before and after the experiment the absorbed amount of chlorine was determined that is its distribution in a single length of the adsorbing layer.

5. Occasionally we have confirmed the characteristic approximate relation, namely $C_0 \times T = K$, where C_0 is the initial concentration of the chlorine, T is the service time of a definite charcoal layer and K is a constant.

We have carried out all these series of experiments at different initial concentrations of chlorine and air stream velocities, as well as with different kinds of charcoal, as is specified in the descriptions of individual experiments in the following

II. Experimental part

A. Experiments on the distribution of chlorine in the air inside the adsorbing layer at the moment of the exhaustion of the protective action.

No. of gas measuring flasks or bed layers (= layer lengths in decimeters)	Amount of adsorbed chlorine in grams	Service Time	Concentration of chlorine in the air stream in % of the initial quantity
--	--------------------------------------	--------------	--

1. Velocity of the air stream 3 liters/min.
Activated "normal" charcoal (dry, 10 mm. grain size).

(a) Initial chlorine concentration 2.2%.
(Fig. 1 No. 2; Fig. 2 No. 1; Fig. 3 No. 8; Fig. 6 No. 8)

1	5.7	61 sec.	100
2	5.4	13 m. 3 s.	95
3	5.0	33 m.	92
4	4.6	61 m.	89
5	3.6	90 m.	82.5
6	2.0	117 m.	59
7	0.8	144 m.	--

(b) Initial concentration 3.96%.
(Fig. 1 No. 3; Fig. 2 No. 2; Fig. 3 No. 2)

1	6.5	28 s.	100
2	6.05	8 m. 30 s.	84
3	5.05	25 m.	90
4	4.17	42 m. 10 s.	81
5	2.75	58 m. 10 s.	61
6	0.48	74 m. 10 s.	14
7	--	90 m.	--

(c) Initial concentration 8.2%.
(Fig. 1 No. 4; Fig. 3 No. 1; Fig. 6 No. 1)

1	--	--	100
2	--	4 m. 12 s.	97.5
3	--	12 m. 24 s.	96.5
4	--	20 m.	95
5	--	29 m.	84
6	--	38 m. 15 s.	59
7	--	46 m. 54 s.	12

2. Velocity of the air stream 5 liters/min.
Normal charcoal.

(a) Initial concentration 0.66%.
(Fig. 3 No. 9)

1	--	1 m.	100
2	--	17 m.	88
3	--	67 m.	82
4	--	116 m.	71
5	--	182 m.	36
6	--	239 m.	--

(b) Initial concentration 0.93%.
(Fig. 3 No. 7; Fig. 6 No. 7)

1	--	31 s.	100
2	--	13 m. 20 s.	99
3	--	34 m. 45 s.	94
4	--	70 m. 47 s.	93
5	--	98 m. 7 s.	74
6	--	132 m. 20 s.	41
7	--	166 m. 30 s.	--

(c) Initial concentration 1.36%.
(Fig. 4 No. 2)

1	--	--	100
2	--	8 m.	96
3	--	27 m.	91
4	--	49 m. 30 s.	83
5	--	76 m.	58
6	--	* 89 m.	--
7	--	* 115 m.	--

* Misprint in German text - corrected from Russian cf. Z. Elektrochem
52, 96 (1930)

- (d) Initial concentration 1.93%.
(Fig. 2 No. 5; Fig. 4 No. 1; Fig. 3 No. 4; Fig. 6 No. 4)

1	5.21	23 s.	100
2	4.73	5 m. 50 s.	97
3	3.97	17 m. 34 s.	--
4	3.69	33 m. 50 s.	92
5	2.84	52 m. 40 s.	87
6	1.19	71 m. 26 s.	47
7	0.20	88 m.	--

- (e) Coarse grained charcoal (16 mm. diameter)
Velocity of air stream 3 liters/min.
Initial concentration 2.13%.
(Fig. 1 No. 6; Fig. 2 No. 4; Fig. 3 No. 5; Fig. 6 No. 6)

1	4.9	20 s.	100
2	4.8	4 m.	97
3	4.3	18 m. 20 s.	93
4	4.1	45 m. 54 s.	87
5	2.7	66 m.	73
6	1.0	92 m. 30 s.	47
7	-	121 m.	6
8	-	143 m.	--

- (f) Mildly activated charcoal.
Velocity of air stream 3 liters/min.
Initial concentration 2.2%
(Fig. 1 No. 1; Fig. 3 No. 3; Fig. 6 No. 2)

1	1.9	20 s.	100
2	1.9	4 m. 54 s.	93
3	1.9	12 m. 54 s.	91
4	-	22 m. 30 s.	88
5	1.9	34 m.	87
6	1.4	45 m. 30 s.	65
7	0.5	56 m. 30 s.	16
8	-	57 m. 30 s.	--

- (g) Non-activated charcoal.
Velocity of the air stream 3 liters/min.
Initial concentration 2.0%
(Fig. 1 No. 5; Fig. 2 No. 3; Fig. 3 No. 2; Fig. 6 No. 3)

1	--	10 s.	100
2	--	3 m. 45 s.	95
3	--	12 m. 45 s.	90
4	--	23 m.	--
5	--	31 m. 45 s.	87
6	-	40 m.	49
7	--	50 m. 10 s.	15

- (h) Charcoal with 18% moisture.
Velocity of the air stream 3 liters/min.
Initial concentration 2.2%.
(Fig. 2 No. 10)

1	--	1 m. 8 s.	100
2	--	18 m. 30 s.	94
3	--	47 m. 20 s.	89.5
4	--	84 m. 7 s.	--
5	--	120 m.	87
6	--	155 m.	67
7	--	189 m. 30 s.	14

B. Series of experiments to determine the change of the chlorine concentration in the air inside the adsorbing layer with time.

Time in minutes	After the 1st layer in % of init. conc.	After the 2nd layer in % of init. conc.	After the 3rd layer in % of init. conc.
-----------------	---	---	---

1. Velocity of the air stream 3 liters/min.
Initial concentration 2.0%.
(Fig. 5 Nos. 4, 6, 8)

10	14	0.5	--
15	24	--	0.23
20	38	10	--
25	45.5	--	--
30	60	30	8
35	69	--	--
40	81.5	51	--
45	--	--	31
50	--	66	--
55	88	--	--
60	--	82	58
65	94	--	--
75	--	--	71
90	--	87	--
115	96	--	--
120	--	--	84
130	--	94	--
135	--	--	87

2. Velocity of the air stream 3 liters/min.
Initial concentration 3.98% chlorine (Fig. 7).

5	3	-	-
10	14	3	-
15	32	12	2
20	50	35	-
25	66	43	-

30	77	58	33
35	90	66	--
40	97	78	--
45	--	90	69
50	98	--	--
60	--	--	88
85	--	98	--
90	--	--	97

3. Non-activated charcoal.

Velocity of the air stream 3 liters/min.

Chlorine concentration 2%. (Fig. 5 Nos. 1, 2, 3).

5	32	19	14
10	60	47	32
15	80	60	51
20	88	82	72
25	92	--	80
30	--	89	88
35	94	--	--
40	94	91	--
45	--	--	90
50	--	--	--

4. Charcoal with 18% moisture.

Velocity of the air stream 3 liters/min.

Chlorine concentration 2%. (Fig. 5 Nos. 5, 7, 9.)

10	8.8	--	--
15	28.9	--	--
20	50.5	5	--
25	58.8	--	--
30	67.2	34	6
35	72	--	--
40	82.3	54	--
45	84.8	--	26
50	88.8	69	--
55	93.2	--	--
60	--	82	60
70	--	85	--
75	--	--	72
80	--	90	--
90	--	94	80
105	--	--	82

2. Series of experiments to verify the relations: $C_0 \times T = K$.

Length of the adsorb. layer.	Chlorine concentration		
	1.00%	0.56%	1.36%
20	13	12	11
30	34	44	37
40	70	77	67
50	98	--	103
60	113	125	121
70	166	--	157

In columns 2, 3, 4 of the table the values of $C_0 \times T$ are given.

3. Discussion of the Experimental Results

The graphic representation (cf. the accompanying figures) of the spatial distribution of the adsorbed chlorine in the charcoal sections of the residual chlorine in the gas phase, as well as of the time lapses of the adsorption process is given in the characteristically inflected curves. They show clearly, as W. Mecklenberg emphasized, that the adsorption capacity of the charcoal section in the direction of the stream remains partially unused. This fact plays an essential part, when the efficiency of a given quantity of adsorbent is considered, however there are other points of importance for the complete picture of the phenomenon and its course in time which we will consider purely empirically without calculating the absolute magnitudes.

The concentration of the chlorine remaining in the gas phase inside the charcoal section will decrease regularly from the initial concentration at the entrance of the apparatus to zero at the point, where the chlorine no longer appears because of complete adsorption. The dimensions of the domain which corresponds to this gradient, that is the curve of falling off of the chlorine concentration inside the charcoal, can be expressed in length- as

Well as time- units, because we have to deal with a certain velocity of the progress of the chlorine³ along the adsorbing layer. We will therefore use

³

It is self evident that it is really not a gradient curve but a gradient area for the advance of the chlorine through the charcoal bed that is meant. The expression "curve" is therefore to be understood in the sense of the mean of this area in the direction of the length of the charcoal bed.

the time units.

In the last spaces of the charcoal layer, the gradient curve forms under the same conditions as in the middle⁴ spaces; the chlorine concentration

⁴

We leave the accidental passage of the chlorine to the end of the charcoal bed outside consideration. This will in fact not be indicated by the test paper present at the end; the visible blue colour shows up only after the gradual appearance of the chlorine outside the charcoal bed.

increases gradually at each point from zero to the initial concentration, and this occurs in the bulk as the adsorption capacity of the space in question as well as the preceding ones are saturated. Exactly the same may be observed by the appearance of gas at the end of the adsorbing layer: this same gradient curve appears temporarily with small changes at different parts of the bed (cf. diagram). At the beginning of the adsorbing layer (where the gas enters) the relation is different from all the others, because at this point and only at this point the gradient curve does not gradually build up from a concentration equal to zero, but from the first moment of the experiment has a value equal to the initial concentration of the gas and remains constant at this maximum. Consequently the building up of the gradient curve at the beginning of the adsorbent bed follows a course so that the velocity of the advance of the gas appears greater than in the remaining parts of the bed and therefore the corresponding duration of the protective action at the beginning of the experiment in comparison with

the later stages. Only after the gradient curve is built up, can its regular advance with a constant velocity in the direction of the bed be assumed.

Of course such a conception is only to be regarded as approximate. In reality as our experiments show, the gradient curve is appreciably deformed by the advance and moreover a complete saturation of the adsorption capacity of the apparently used up part of the charcoal bed does not occur, but this continues adsorbing more, if only in small quantity. It can therefore be imagined that instead of a parallel displacement of the gradient curve, it undergoes a change of its configuration with time, where^{by} the point O on the ordinate axis, which corresponds to the initial concentration, can be considered as the starting point of all the curves, as is represented schematically in Fig. 8. Actually the quadrilaterals OAB, OBC, OCD, etc. at a definite place in the figure can be assumed to be approximately of equal size. The quadrilaterals correspond to the adsorbed amount of gas related to a definite length of the adsorbing bed and each single one corresponds also to an approximately constant service time, that is to an approximately equal time of gas protective action. This corresponds to the stretches of the curves in Fig. 3 running rectilinearly, which show the dependence of the service time on the length of the adsorbing section. The initial sections of the corresponding curves in Fig. 3 show a curve which corresponds to the smaller quadrilaterals OPQ, OQR, etc. in Fig. 8. It is therefore consistent that at the beginning of the adsorbing layer or in the first period of the adsorption the adsorptive power of the charcoal layer is exhausted relatively quickly, since the later ones correspond to a constant, maximum (initial) concentration of the adsorbable gas. The service time of the initial sections of the adsorbing layer, related to a unit of length, is therefore^a shorter one in comparison to the middle or end sections, although the

greatest amount of chlorine is adsorbed on the initial lengths, because these lengths can adsorb more after the expiration of their service time. It is thence also understood that the curves which represent the distribution of the adsorbed chlorine in the charcoal bed have a reverse slope to the curves which represent the dependence of the service time on the length of the charcoal bed (cf. Fig. 2 and 3).

In fact we have observed experimentally by our method of procedure that a constant service time is obtained with a given tube from the following ones. The last tube of the series is no exception on the other hand we find for the first two or three tubes a shorter period of protective action, corresponding to the faster progress of the adsorption at the beginning of the bed, where a constantly higher concentration (initial concentration) of the chlorine in the air stream prevails.

Now take the relation

$$\frac{\text{Service time}}{\text{Length of the adsorbing bed}} = \frac{T}{L} = \mathcal{V}$$

where \mathcal{V} equals "the coefficient of protective action". Let us consider the difference of the service times for a fixed length, one time reckoned from the beginning of the bed and the other time in the central parts of the bed and make the assumption, that in the second case the chosen range corresponds to a complete formation of the gradient curve, that is the rectilinear course of the curves in Fig. 3. This difference, which as the difference between two real time intervals has a real meaning, is further symbolized with τ , "the initial service waste". Both quantities \mathcal{V} and τ can be determined without

difficulty experimentally and allow the properties of an adsorbent bed to be defined empirically for fixed experimental conditions and further the service time to be calculated from the length of the adsorbing bed. Thus our method of representation is also of practical importance.

We have carried out this calculation for the experiment given above and have obtained satisfactory agreement with the experimental numbers. γ was determined from the service time of a length of charcoal bed in the front (lying down stream) part of the apparatus divided by the length of this chosen section. γ' appears as the difference between the service times of equal lengths of the charcoal bed at the beginning and end of the adsorption apparatus.

1. Air flow 3 liters, chlorine concentration 2.2%

$$\tau = 50 \text{ m. } \gamma = 2.77 \text{ m.}$$

L = 70 cm.	T* = 143.9 m.	144 m.
60	116.2	117
50	88.5	90

2. Air flow 3 liters, chlorine concentration 3.98%

$$\tau = 94 \text{ m. } \gamma = 1.65 \text{ m.}$$

L = 60 cm.	T = 75 m.	74.5 m.
50	58.5	56.5
70	91.5	90

* In the first column the observed and in the second the calculated values are given.

3. Air flow 3 liters, chlorine concentration 0.2%

$$\tau = 16 \text{ m. } \mathcal{G} = 0.9 \text{ m.}$$

L = 50 cm.	T = 29 m.	29 m.
60	38	38.25
70	47	46.9

4. Air flow 5 liters, chlorine concentration 0.93%

$$\tau = 64 \text{ m. } \mathcal{G} = 3.3 \text{ m.}$$

L = 50 cm.	T = 101 m.	98.1 m.
60	134	132
70	167	166.5

5. Air flow 5 liters, chlorine concentration 1.92%

$$\tau = 36.7 \text{ m. } \mathcal{G} = 1.76 \text{ m.}$$

L = 50 cm.	T = 52.3 m.	52.6 m.
60	69	71
70	86.5	88

6. Air flow 5 liters, chlorine concentration 0.66%

$$\tau = 98 \text{ m. } \mathcal{G} = 5.5 \text{ m.}$$

L = 50 cm.	T = 177 m.	182 m.
60	242	239

The dependability of the quantities \mathcal{G} and τ on the experimental conditions is illustrated by the following numbers:

Air flow 3 liters	τ	\mathcal{G}
Chlorine concentration 2%	50	2.77
	4	1.65
	8	0.9

Air flow 5 liters

Chlorine concentration 0.66%	98	5.5
1.00	64	3.3
2.00	37	1.76

Non-activated charcoal: $\tau = 13$; $\mathcal{V} = 0.9$

Coarse-grained charcoal: $\tau = 64$; $\mathcal{V} = 2.66$

Both with air flow of 3 liters.

In conclusion we might point out, that the quantities \mathcal{V} and τ introduced by us stand in direct relationship with the "dead space" of Mecklenberg. From Fig. 9 it may be seen, that the "dead space" of Mecklenberg is represented by the line OA. The quantity τ is on the other hand equal to $O'O = AB$. From which flows $OA = AB \tan \phi$ or the "dead space" = τ/\mathcal{V} , because \mathcal{V} as quotient T/L (Inverse velocity coefficient) is put equal to $1/\tan \phi$. From this the "dead space" of Mecklenberg acquires a definite physical meaning, instead of being a "mathematical fiction"⁵.

⁵

Moscow, December 1928. Inorganic Chemistry laboratory of the Technical High School. Kolloid-Z. 49, 288 (1929)

it means namely that a time interval is expressed in units of length with the help of an inverse velocity coefficient. In other words it specifies the length of the adsorbing bed, which would correspond to the time interval of the initial waste of the protective power (τ), if the coefficient of protective action (\mathcal{V}) were constant during the whole experiment.

Summary.

The distribution of the chlorine adsorbed by an adsorbing bed from an air stream, as well as the distribution of the residual chlorine in the gas phase along the same bed in a specially constructed apparatus was studied.

The dependence of the service time on the length of the adsorbing bed is expressed by two empirical quantities. These quantities permit the definition of the adsorption properties of a bed under fixed experimental conditions and the calculation of the service time for different bed lengths under the same conditions.

Moscow, December 1928. Inorganic Chemistry Laboratory of the Technical High School. Kolloid-Z. 49, 238 (1929).

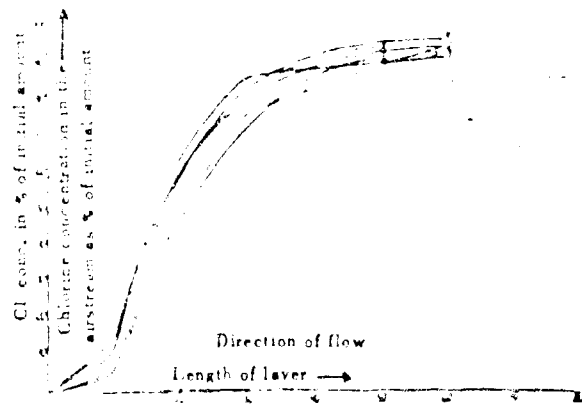


Fig. 1. N1 Airstream 3 l. Cl. conc. 2.22% weakly activated charcoal.
 N2 " " " " 2.2 normally activated charcoal
 N3 " " " " 3.98 " " "
 N4 " " " " 8.2 " " "
 N5 " " " " 2 non-activated "
 N6 " " " " 2.13 coarse grain "

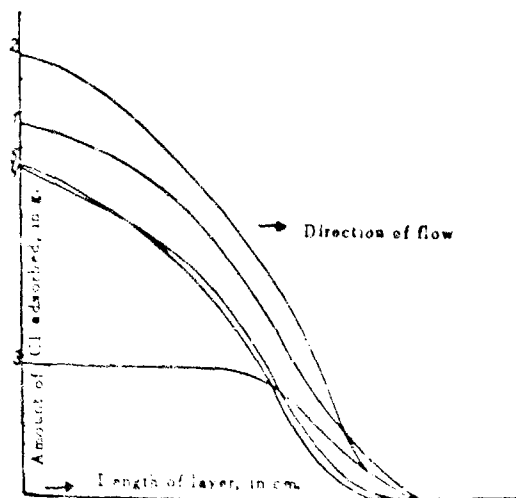


Fig. 2. Airstream 3 l. per min.
 N1 Cl concentration 2.2% normally activated charcoal
 N2 " " 3.98 " " "
 N3 " " 2.22 non-activated "
 N4 " " 2.13 coarse grain "

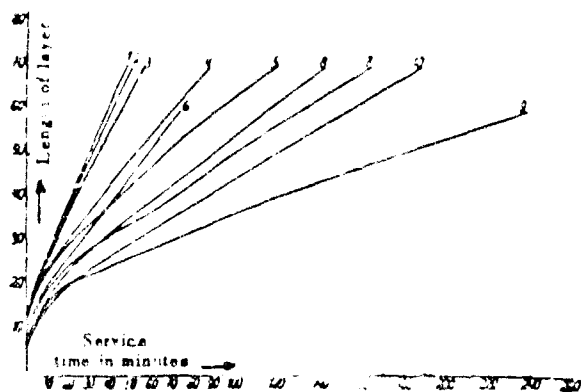


Fig. 3. N1 Airstream 3 l. Cl conc. 8.2% normally activated charcoal

N2	"	"	"	2	non-activated	"
N3	"	"	"	2.22	weakly activated	"
N4	"	5 l.	"	1.9	normally	"
N5	"	3 l.	"	2.13	coarse grained	"
N6	"	"	"	3.98	normally activated	"
N7	"	5 l.	"	0.9	"	"
N8	"	3 l.	"	2.2	"	"
N9	"	5 l.	"	0.6	"	"
N10	"	3 l.	"	2	moistened	" (18%)

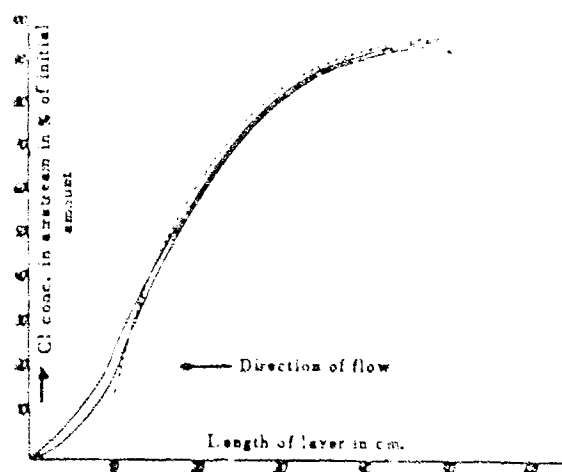


Fig. 4. Airstream 5 l. per min.
N1 Cl conc. 1.9%
N2 " " 1.36%
Dotted line is taken from Fig. 1 (3 l. per min.)

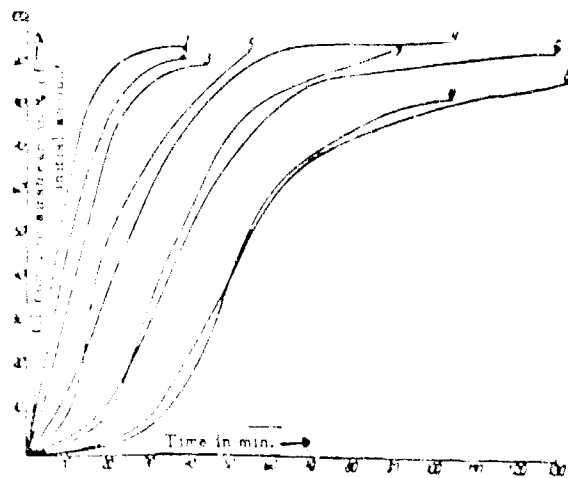


Fig. 5. Non-activated charcoal

Airflow 3 l. per min.
Cl conc. 2%

Charcoal with 18%
moisture, airflow 3 l.
per min. Cl conc. 2%

Normal charcoal
Airstream 3 l. per min.
Cl conc. 2%

N1 after 1st observed length

N2 " 2nd " "

N3 " 3rd " "

N5 " 1st " "

N7 " 2nd " "

N9 " 3rd " "

N4 " 1st " "

N6 " 2nd " "

N8 " 3rd " "

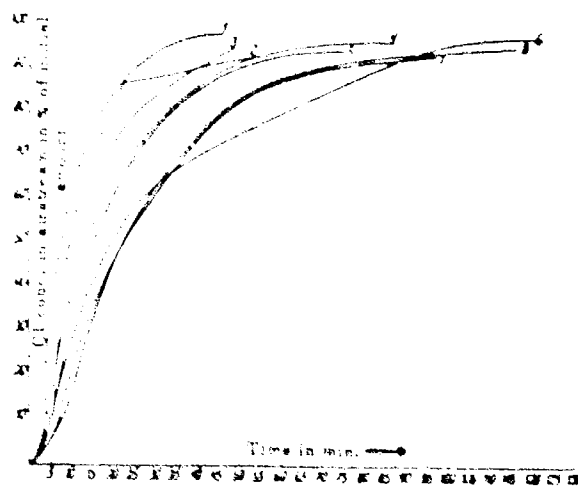


Fig. 6. N1 airflow 3 l. Cl conc. 8.2% normally activated charcoal

N1	"	"	"	0.22	weakly	"
N2	"	"	"	2	non-activated	"
N3	"	5 l.	"	1.2	normally activated	"
N4	"	3 l.	"	3.03	"	"
N5	"	"	"	2.13	coarse grained	"
N6	"	5 l.	"	0.93	normally activated	"
N7	"	3 l.	"	2.1	"	"

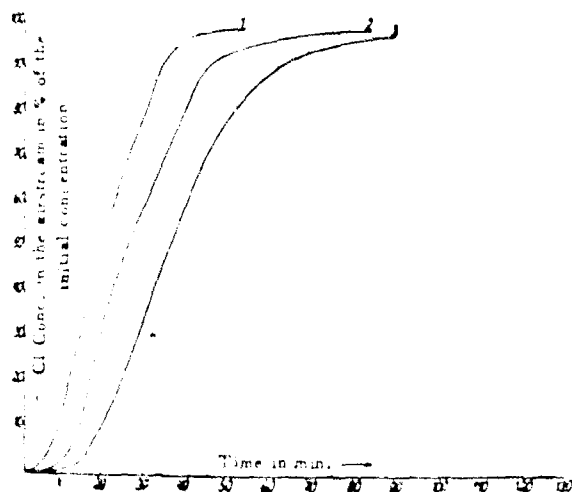


Fig. 7. Air flow 5 ft. per min.
Cl concn. 0.98%

N1 after 1st observed length
N2 " and " "
N3 " and " "

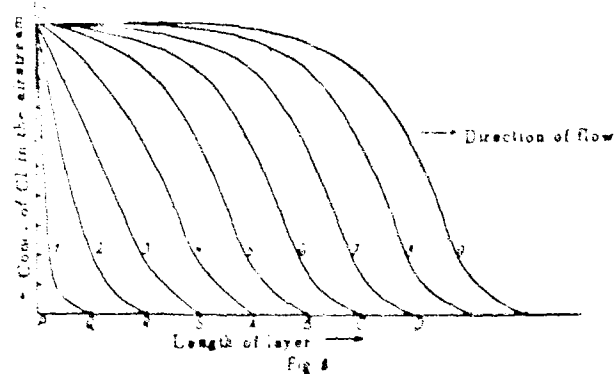


Fig. 8

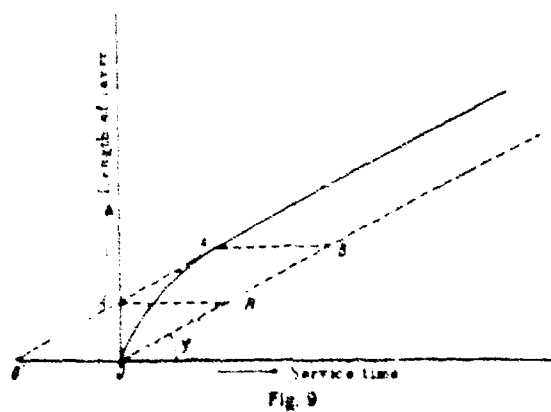


Fig. 9